(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 916 388 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
19.05.1999 Bulletin 1999/20

(51) Int Cl.[6]: **B01D 53/86**

(21) Application number: **98309136.4**

(22) Date of filing: **09.11.1998**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **14.11.1997 JP 313089/97**
27.05.1998 JP 145748/98

(71) Applicants:
- **Hitachi, Ltd.**
 Chiyoda-ku, Tokyo 101-8010 (JP)
- **Hitachi Engineering Co., Ltd.**
 Hitachi-shi, Ibaraki 317-0073 (JP)
- **Hitachi Kyowa Engineering Co., Ltd.**
 Hitachi-shi, Ibaraki 317-0072 (JP)

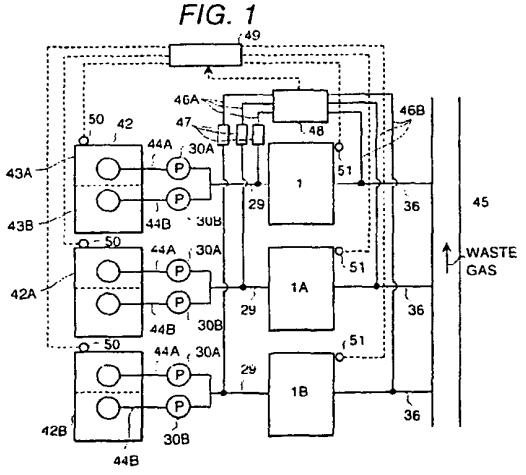
(72) Inventors:
- **Irie, Kazuyoshi**
 Hitachi-shi, Ibaraki 317-0077 (JP)
- **Mori, Toshihiro**
 Naka-gun, Ibaraki 319-1112 (JP)
- **Yokoyama, Hisao**
 Hitachioota-shi, Ibaraka 313-0038 (JP)
- **Tomiyama, Takayuki**
 2-chome, Hitachi-shi, Ibaraki 316-0004 (JP)
- **Takano, Toshihide**
 Nishiibaraki-gun, Ibaraki 309-1738 (JP)
- **Tamata, Shin**
 Higashiibaraki-gun, Ibaraki 311-1301 (JP)
- **Kanno, Shuichi**
 Hitachi-shi, Ibaraki 319-1225 (JP)

(74) Representative: **Hackney, Nigel John et al**
Mewburn Ellis,
York House,
23 Kingsway
London WC2B 6HP (GB)

(54) A method for processing perfluorocarbon and an apparatus therefor

(57) An exhaust gas containing a perfluoride compound (PFC) and SiF_4 is conducted into a silicon remover and contacted with water. A reaction water supplied from a water supplying piping and air supplied from an air supplying piping are mixed with the exhaust gas exhausted from the silicon remover. The exhaust gas containing water, air, and CF_4 is heated at 700 °C by a heater. The exhaust gas containing PFC is conducted to a catalyst layer filled with an alumina group catalyst. The PFC is decomposed to HF and CO_2 by the catalyst. The exhaust gas containing HF and CO_2 at a high temperature exhausted from the catalyst layer is cooled in a cooling apparatus. Subsequently, the exhaust gas is conducted to an acidic gas removing apparatus to remove HF. In accordance with the present invention, the silicon component is removed from the exhaust gas before introducing the exhaust gas into the catalyst layer. Therefore, surface of the catalyst can be utilized effectively, and the decomposition reaction of the perfluoride compound can be improved.

FIG. 1



EP 0 916 388 A2

C_2F_6 is 9,200 times, and SF_6 is 23,900 times. Therefore, although PFC has a smaller releasing amount than CO_2 which is required to be decreased as a cause of warming-up the earth, release of the PFC is anticipated to be certainly restricted in near future. In this case, a countermeasure against the exhaust gas from semiconductor manufacturing plants, which occupies a majority of the PFC releasing amount, will become important.

[0007] For instance, in accordance with an etching step in the semiconductor manufacturing plant, a PFC gas for etching is supplied into a chamber. A part of the PFC gas is converted to highly corrosive fluorine atoms by applying plasma. The fluorine atoms perform an etching of silicone wafers. The exhaust gas from the chamber is pumped out continuously by a vacuum pump. In order to prevent corrosion by the acidic gas, purging of the exhaust gas with nitrogen gas is performed. The exhaust gas contains nitrogen of 99%, and the PFC of residual 1%, which has not been used for the etching. The exhaust gas pumped out by the vacuum pump is conducted to an acid removing apparatus through the duct for removing the acidic gas, and released to atmosphere as a state containing the PFC.

[0008] In the semiconductor manufacturing plants, a reagent method and a combustion method have been used practically as a decomposition method of the PFC. The former is a method, wherein fluorine is chemically fixed at approximately 400 ~ 900 °C by using a special reagent. In accordance with this method, an exhaust gas processing is not necessary, because any of acidic gas is not generated by decomposition. The latter is a method, wherein the PFC gas is conducted to a combustor, and decomposed thermally in a flame at least 1,000 °C generated by combustion of LPG and propane gas.

[0009] In accordance with the above reagent method, the reagent reacted chemically with the PFC can not be re-used, and the expensive reagent, which is consumed in the reaction as a consumable article, is required to be supplied frequently. Therefore, the operation cost is 10 to 20 times in comparison with the combustion method. Furthermore, because an amount of the reagent equivalent to the amount of the PFC to be processed is necessary, a practical equipment for the reagent method requires a large installing area such as approximately 3 ~ 5 m^2.

[0010] In accordance with the above combustion method, the thermal decomposition is performed at a high temperature such as at least 1,000 °C for C_2F_6 and at least 1,100 °C for CF_4, and a large amount of thermal energy is required. Furthermore, the combustion method generates NOx and a large amount of CO_2 by combustion at a high temperature. Because the PFC is exhausted in a state diluted with inactive N_2 gas, a potential of miss-fire is high, and a sufficient operation control is required.

[0011] An application of the combustion method to the semiconductor manufacturing process has been studied. The PFC is exhausted as a mixed gas diluted with N2 gas to be a concentration of a several %. Accordingly, in combustion of the mixed gas, a large amount of air for combustion is required in addition to a fuel gas. Consequently, because the amount of gas to be processed is increased, size of the apparatus is increased, and the installing area for the apparatus is required to be as large as approximately 0.7 ~ 5 m^2.

[0012] For instance, when C_2F_6 is contained by 1 % in an exhaust gas exhausted by 100 liter/min. from a semiconductor manufacturing process, a necessary amount of LPG to make the thermal decomposition temperature at least 1,000 °C is 10 liter/min. and a necessary amount of air is approximately 400 liter/min. with an excessive ratio of 1.5. The total amount of the exhaust gas after the combustion becomes approximately 500 liter/min., because oxygen in the air is consumed and CO_2 is generated by 30 liter/min. The total amount of the exhaust gas is increased almost 5 times of the exhaust gas exhausted from the semiconductor manufacturing process. The semiconductor manufacturing plant has a large restriction in space, because the plant must be clean rooms. Accordingly, it is difficult to keep the necessary area for installing a new exhaust gas processing apparatus in a previously built semiconductor manufacturing plant.

[0013] On the other hand, a catalytic method, wherein the PFC is decomposed at approximately 400 °C, is applied to CFC (chlorofluorocarbon) and HCFC (hydrochlorofluorocarbon), which have similar chemical compositions with the PFC and an ozone destruction effect. Because the CFC and HFC contain chlorine atoms having a large atomic radius in their compositions, the molecular structures composed by bonding fluorine atoms and hydrogen atoms having a small atomic radius are distorted. Therefore, the CFC and HFC can be decomposed at a relatively low temperature.

[0014] A method for decomposing CFC (or HFC) using a catalyst was disclosed in JP-A-9-880 (1997). In accordance with the above method, a mixed gas of heated air, which is a carrier gas, steam, and CFC is conducted to a catalyst layer. The temperature of the catalyst layer is approximately 430 °C, because CFC has a low decomposition temperature. The exhaust gas containing decomposed gases exhausted out from the catalyst layer is cooled rapidly with cooling water, because of preventing generation of dioxine.

[0015] Preferably the present invention provides a method for processing perfluorocarbon using a catalyst, which can improve the decomposition reaction, and an apparatus therefor.

[0016] The first aspect of the invention is in the steps of removing silicon components from an exhaust gas containing a perfluoride compound and the silicon components, subsequently, supplying the exhaust gas containing the perfluoride compound, to which any of water or steam is added, to a catalyst layer which is filled with a catalyst, to decompose the perfluoride compound with the catalyst.

[0017] In accordance with the first aspect , closing pores formed on the catalyst by solid particles generated by a

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0024] A perfluoride compound processing apparatus (PFC gas processing apparatus), i.e. a preferred embodiment of the present invention applied to an exhaust gas control system of an etching apparatus in a semiconductor manufacturing plant, is explained hereinafter referring to FIG. 1, FIG. 2, and FIG. 3.

[0025] The PFC does not contain chlorine, its molecular structure is compact, its bonding force is strong, and its decomposition temperature is as high as approximately 700 °C. Therefore, the catalytic method (disclosed in JP-A-9-880 (1997)), which could be applied to the CFC and HFC, could not be applied to the PFC. However, currently, the inventors of the present application have succeeded in development of an alumina group catalyst having a reaction temperature at approximately 700 °C applicable to the decomposition of PFC. Regarding the above catalyst, patent applications are filed to the Japanese Patent Office as Japanese Patent Applications No. Hei 9-4349 (filed January 14, 1997) and No. Hei 9-163717 (filed June 20, 1997). In accordance with the present embodiments, the above catalyst are used for processing the exhaust gas.

[0026] In accordance with the exhaust gas control system of the dry etching apparatus, for instance, each of PFC processing apparatus 1, 1A, 1B, is connected to each of three dry etching apparatus 42 as indicated in FIG. 1. Each of the dry etching apparatus 42 comprises two etching regions 43A, 43B, partitioned in the apparatus.

[0027] In each of the etching regions, an etching process is performed for wafers by supplying CF_4, i.e. a PFC gas, as an etching gas. The exhaust gas from the etching regions 43A, 43B, is conducted to a PFC processing apparatus 1 through piping 44A, 44B, 29, by driving vacuum pumps 30A, 30B. The exhaust gas contains approximately 1 % of CF_4, which has not been consumed in the etching process, and SiF_4 generated by the etching process. The exhaust gas is exhausted to the duct 45 after processed in the PFC processing apparatus 1 through the piping 36. The exhausted gases from other dry etching apparatus 42 are also conducted to the duct 45.

[0028] Each of the exhaust gas in the piping 29 and the exhaust gas in the piping 36 is conducted to a gas chromatography by sampling piping of 46A and 46B, respectively. An acid gas filter 47 is provided in the sampling piping 46A. Concentrations of CF_4 in the exhausted gases supplied to and exhausted from the PFC processing apparatus 1 are determined by the chromatography 40. The determined values on the concentration of CF_4 in the exhausted gases are input to a monitoring apparatus 49. When the concentration of CF_4 in the exhausted gas in the piping 36 is higher than a first preset value, the monitoring apparatus 49 generates an alarm sound with flashing a warning device 51 of the corresponding PFC processing apparatus for warning generation of an abnormal state. When the concentration of CF_4 in the exhausted gas in the piping 29 is higher than a second preset value, the monitoring apparatus 49 generates an alarm sound with flashing a warning device 50 of the corresponding dry etching apparatus 42 for warning generation of an abnormal state. Furthermore, the monitoring apparatus 49 checks a normality of the catalytic reaction in the reactor 9, which will be explained later, and a catalyst change timing from deterioration of the catalyst, based on a decomposition ratio obtained from the concentrations of CF_4 at the entrance and the outlet of the PFC processing apparatus 1.

[0029] Next, an approximate arrangement of the above exhaust gas control system in the clean rooms of the semiconductor manufacturing plant is explained hereinafter referring to FIG. 2. A building 59 of the semiconductor manufacturing plant is composed of clean rooms 53, 54, at both an upper side and a lower side of grating 52, respectively. Air in the clean room 54 is cleaned by filters 55A, 55B, and conducted to the clean room 53 through the piping 57A, 57B, by driving blowers 55A, 55B. The air is cleaned again by the filter 58. The clean room 53 has a higher cleanliness than the clean room 54. The dry etching apparatus 42 is installed in the clean room 53, i.e. a manufacturing apparatus area. The PFC processing apparatus 1, 1A, and the like, and the vacuum pumps 30A, 30B, are installed in the auxiliary apparatus area in the clean room 54. The piping such as piping 44A, duct 45, and the like are arranged at the piping area above the auxiliary apparatus area in the clean room 54.

[0030] A composition of the PFC processing apparatus is explained hereinafter referring to FIG. 3. The compositions of the PFC processing apparatus 1A, 1B, are as same as the composition of the PFC processing apparatus 1. The PFC processing apparatus comprises a silicon remover 2, a heating apparatus 3, a reactor containing a catalyst layer 11, a cooling apparatus 22, an acidic gas removing apparatus 98, a blower 59, a waste water pump 60, and a temperature controller 62. The exhaust gas exhausted from the blower 30A is conducted to the duct 45 through the silicon remover 2, the heating apparatus 3, the reactor, the cooling apparatus 22, the acidic gas removing apparatus 98, and the blower 59. The heating apparatus 3, the reactor 9, and the cooling apparatus 22 are assembled in an integral body as indicated in FIG. 5, and composed of a PFC decomposition processing unit 76.

[0031] A detailed composition of the silicon remover 2 is indicated in FIG. 4. The silicon remover 2 comprises a spray 26 and a diffusion portion 27 filled with packing materials inside its vessel. The exhaust gas containing CF_4, SiF_4, and the like as impurities is conducted into the vessel of the silicon remover 2 via the piping 29. The exhaust gas outlet of the piping 29 in the vessel is oriented downwards. The exhaust gas flows upwards in the vessel, and passes through the diffusion portion 27 to diffuse and to flow in the vessel. Cooling water supplied from a water supplying pipe 38 is sprayed through the spray 26. The diffusion portion 27 increases a contacting ratio of the sprayed water and the exhaust

[0041] The heated exhaust gas containing CF_4 is supplied to the reactor 9 filled with the catalyst. The CF_4 in the exhaust gas is reacted with H_2O and decomposed to HF and CO_2 by the effect of the alumina group catalyst in the catalyst layer 11 as expressed by the following equation (2):

$$CF_4 + 2H_2O \Rightarrow CO_2 + 4HF \quad (2)$$

[0042] In a case when C_2F_6, one of the PFC, is contained in the exhaust gas, C_2F_6 is decomposed to CO_2 and HF by the reaction expressed by the following equation (3):

$$C_2F_6 + 2H_2O \Rightarrow 2CO_2 + 6HF \quad (3)$$

FIG. 6 is a graph indicating decomposition characteristics of the PFC by the alumina group catalyst, and the abscissa indicates decomposition temperature and the ordinate indicates decomposition rate. The alumina group catalyst used in the measurement had the composition explained previously. Tested gases were four kinds of PFC, such as CHF_3, CF_4, C_2F_6, and C_4F_8. As the testing conditions, the concentration of respective PFC was 0.5 %, and SV was 1000/h. The reaction water was added approximately 10 times of a theoretical amount. As FIG. 6 reveals, all the four PFC indicated the decomposition rate near 100 % at a reaction temperature of approximately 700 °C. The decomposition rate of CF_4 and CHF_3 at approximately 650 °C is equal to or more than 95 %, and the decomposition rate of C_2F_6 and C_4F_8 at approximately 670 °C is equal to or more than 80 %. By using the above catalysts, practical decomposition of the PFC in the range of approximately 650 ~ 750 °C become possible.

[0043] The high temperature exhaust gas containing the decomposed gases such as CO_2 and HF exhausted from the catalyst layer 11 is conducted to the cooling region 23 in the cooling apparatus 22 through the baffle 20.

[0044] The cooling water supplied throughout he water supplying piping 39, and 40 are sprayed continuously in to the cooling region 23 by the sprays 24 and 25. The exhaust gas at a high temperature is cooled to 100 °C or lower by the sprayed water. A part of HF is removed from the exhaust gas by dissolving into the cooling water. The cooling of the exhaust gas at a high temperature can be achieved not by spraying but by bubbling the gas into a water tank. The sprayed water is conducted to a lower portion of the acidic gas removing apparatus 98 through the piping 34 and 35. In accordance with the provided baffle 20, the path for conducting the exhaust gas from the baffle holder 21 to the cooling apparatus 22 becomes zigzag, and a back flow of the splashed cooling water sprayed from the sprays 24 and 25 into the catalyst layer 11 can be prevented. Therefore, a temperature drop of the catalyst layer 11 by the splashed water can be prevented, and release of undecomposed PHC can be avoided.

[0045] The exhaust gas containing the decomposed gases (CO_2 and HF) at a low temperature exhausted from the cooling apparatus 22 is conducted to the acidic gas removing apparatus 98 through the piping 33. The acidic gas removing apparatus 98 comprises a packed layer 95 filled with Raschig rings made of plastics and a spray 27 inside for removing HF contained in the decomposed gas by a high concentration such as approximately 4 % by volume. The spray 27 is arranged at above the packed layer 95. The cooling water supplied through the water supply piping 70 is sprayed through the spray 27. The cooling water is flowed down through the packed layer 95. The exhaust gas is contacted sufficiently with the cooling water in the packed layer 95, and a majority of the HF contained in the exhaust gas can be dissolved into the cooling water. The HF in the exhaust gas can be removed significantly by the acidic gas removing apparatus 98 from 4 % by volume to a several ppm.

[0046] The exhaust gas, of which acidic gas content is decreased remarkably, is conducted to the duct 45 through the piping 36 by operating a blower 59, and released outside the system. Inside the cooling apparatus 22 and the acidic gas removing apparatus 98 are kept at a negative pressure by the operation of the blower 59. Leaking the hazardous HF contained in the exhaust gas to outside the system can be prevented. The bubbling method also can be applied to the acidic gas removing apparatus 98. However, in accordance with the spraying method, a pressure loss is smaller than the bubbling method, and the capacity of the blower 59 can be made small.

[0047] The waste water generated at the silicon removing apparatus 2, the cooling apparatus 22, and the acidic gas removing apparatus 98 are gathered together once at a lower portion of the acidic gas removing apparatus 98. The waste water contains impurities such as SiO_2, HF, and others. The waste water is conducted to a neutralizer (not shown in the drawing) though the piping 37 by operating the waste water pump 60, and processed. In accordance with the present embodiment, the solid particles such as SiO_2 are not brought into the catalyst layer 11 in the reactor 3, because the silicon components contained in the exhaust gas are previously removed by the silicon remover 2 as SiO_2. If the silicon remover 2 is not arranged, SiO_2 is generated by the reaction expressed by the equation (1) with the water supplied from the water supplying piping 32 at a portion in a downstream from the joining point of the piping 31 and the water supplying piping 32. When the SiO_2 is flowed into the catalyst layer 11, the following problems (1) and (2)

and a return piping 75 is newly added. The silicon removing apparatus 71 comprises silicon removers 2 and 22. The silicon remover 72 comprises a spray 73, and a diffusion portion 74 filled with packing materials inside its vessel. The silicon remover 72 has a same composition as the silicon remover 2 indicated in FIG. 4. An outlet of the piping 29 is oriented downwards in the silicon remover 72. The ball check valve 27 is not provided at the outlet side of the silicon remover 72. The return piping 75 is connected to the piping 37 in the downstream of the waste water pump 60. The vessel of the silicon remover 72 is composed of corrosion resistant vinyl chloride, in order to prevent corrosion by HF.

[0057] The exhaust gas containing CF_4, SiF_4, and the like is conducted into the vessel of the silicon remover 72 through the piping 29. The exhaust gas ascends in the vessel, and flows inside the vessel by diffusion through the diffusion portion 74. A part of waste water pumped out by the waste water pump 60 is sprayed through the spray 73 through the return piping 75. Concentration of respective F ions and Si ions in the waste water pumped out from the waste water pump 60 are less than tens ppm. The waste water has a sufficient performance for removing the Si and HF. In accordance with contacting a part of SiF_4 contained in the exhaust gas with the sprayed waste water, the reaction expressed by the equation (1) occurs. The generated SiO_2 is removed from the exhaust gas by the waste water. The HF is dissolved into the waste water.

[0058] The exhaust gas exhausted from the silicon remover 72 is conducted to the silicon remover 2. Fresh water supplied through the water supply piping 38 is sprayed through the spray 26 of the silicon remover 2 . In accordance with contacting the residual SiF_4 contained in the exhaust gas with the sprayed water, the reaction expressed by the equation (1) occurs in the silicon remover 2. The waste water containing the SiO_2 and HF is conducted to the silicon remover 72 and mixed with the sprayed waste water from the spray 73. The mixed waste water is conducted to the bottom portion of the acidic gas removing apparatus 98 through the piping 35. The processes at other portions of the PFC processing apparatus 1C is as same as the processing in the PFC processing apparatus 1.

[0059] The PFC processing apparatus 1C generates the same advantages as the advantages obtained by the PFC processing apparatus 1. Furthermore, the PFC processing apparatus 1C has additional advantages as follows. That is, because the amount of the fresh water supplied through the water supply piping 38 in the PFC processing apparatus 1C is decreased, the amount of waste water conducted to the neutralizer (not shown in the figure) is decreased. Furthermore, since the reaction expressed by the equation (1) is generated at two portions in the silicon removers 2 and 72, the removing efficiency of the Si components such as SiF_4 and the like contained in the exhaust gas is improved.

[0060] Another embodiment of the PFC decomposition processing unit is indicated in FIG. 9. The PFC decomposition processing unit 76A of the present embodiment comprises a heating apparatus 3A and a reactor 9A. The cylinder 17, the baffle holder 21, and the cooling apparatus 22 of the PFC decomposition processing unit 76 are also used in the PFC decomposition processing unit 76A by being arranged on the flange 13 in the casing 6 in the above order. The reactor 9A comprises a bottom portion 83 in an internal tube 79. A bottom plate 82 is provided at the bottom portion 83 as slidable. The catalyst layer 11 filled with the alumina group catalyst is formed on the bottom plate 82 and the bottom portion 83 in the internal tube 79. The alumina group catalyst is a catalyst containing Al_2O_3 80 % and NiO_2 20 %. A flange 81 of the internal tube 79 is fixed to the flange 13.

[0061] The heating apparatus 3A comprises an internal tube 77, the electric heater 4, and the insulating material 5 covering the electric heater 4. The electric heater 4 and the insulating material 5 are arranged between the internal tube 77 and the casing 6. A flange 78 of the internal tube 77 is fixed to the flange 80. A gap 16 is formed between the casing 6 and the flanges 78 and 81.

[0062] The catalyst which reaches at the end of life can be taken out from inside the internal tube 79 by detaching the cylinder 17, the baffle holder 21, and the cooling apparatus 22, and removing the bottom plate 82. Functions of the heating apparatus 3A and the reactor 9A are as same as the functions of the heating apparatus 3 and the reactor 9 of the PFC decomposition processing unit 76. The same advantages as the PFC decomposition processing unit 76 can be obtained by the PFC decomposition processing unit 76A.

[0063] An exhaust gas control system of the dry etching apparatus in the semiconductor manufacturing plant, whereto the other embodiment of the PFC processing apparatus of the present invention is applied, is explained hereinafter referring to FIG. 10, FIG. 11, and FIG. 12. In accordance with the exhaust gas control system of the present embodiment, plural PFC processing apparatus 1D are arranged in a clean room 54. This part differs from the embodiments indicated in FIG. 1 and FIG. 2. Each of the PFC processing apparatus 1 D is connected to the separated piping 29, respectively.

[0064] A detailed composition of the PFC processing apparatus 1D is indicated in FIG. 11. The PFC processing apparatus 1D is a horizontal type, and comprises the silicon remover 2 and the PFC decomposition processing unit 76B. The silicon remover 2 is connected to the piping 29. The PFC decomposition processing unit 76B comprises the heating apparatus 3, a reactor 9B, and the cooling apparatus 22. The PFC decomposition processing unit 76B does not comprise the acidic gas removing apparatus 98. In accordance with the present embodiment, the acidic gas removing apparatus 98 is provided to the duct 45. The heating apparatus 3 of the PFC decomposition processing unit 76B is composed only by placing the heating apparatus 3 of the PFC decomposition processing unit 76 in a horizontal direction. The reactor 9B comprises plural holding plates 84 and 85, which are perforated with a large number of small holes, in the internal tube 7. The catalyst layer 11 is composed by packing and holding the alumina group catalyst

ducted to the neutralizer can be decreased smaller than that of the PFC processing apparatus 1C.

Claims

1. A method for processing a perfluoride compound comprising the steps of:

 removing silicon components from an exhaust gas containing the perfluoride compound and the silicon components,
 adding at least any of water and steam to said exhaust gas containing the perfluoride compound,
 heating the exhaust gas containing the perfluoride compound, and at least any of water and steam,
 supplying the heated exhaust gas to a catalyst layer filled with a catalyst to decompose the fluoride compound contained in the exhaust gas by contacting with the catalyst,
 cooling the exhaust gas containing decomposed gas generated by the decomposition of the perfluoride compound, and
 releasing the cooled exhaust gas.

2. A method for processing a perfluoride compound as claimed in claim 1, wherein

 said exhaust gas to be supplied to said catalyst layer is controlled to be heated at a designated temperature.

3. A method for processing a perfluoride compound as claimed in claim 2, wherein

 said designated temperature is in the range of 650 °C ~ 750 °C.

4. A method for processing a perfluoride compound as claimed in claim 1, wherein

 an acidic gas is removed from said cooled exhaust gas.

5. A method for processing a perfluoride compound as claimed in claim 1, wherein

 said silicon components is removed from said exhaust gas by contacting the exhaust gas containing said silicon components with water.

6. A method for processing a perfluoride compound as claimed in claim 5, wherein

 said exhaust gas containing the decomposed gas is cooled by heat exchanging said exhaust gas with cooling water.

7. A method for processing a perfluoride compound as claimed in claim 6, wherein

 said removal of the silicon components is performed by using a first silicon component removing apparatus and a second silicon component removing apparatus,
 said exhaust gas exhausted from said first silicon component removing apparatus is supplied to said second silicon component removing apparatus,
 said exhaust gas is contacted with water in the second silicon component removing apparatus, and
 said exhaust gas containing the silicon components is contacted with both waste water from said second silicon component removing apparatus and said cooling water contacted with said exhaust gas containing said decomposed gas in said first silicon component removing apparatus.

8. A method for processing a perfluoride compound as claimed in claim 1, wherein

 said steam is generated by heat exchange of water with said exhaust gas exhausted from said catalyst layer.

9. A method for processing a perfluoride compound as claimed in claim 1, wherein

 said catalyst is an alumina group catalyst.

20. A perfluoride compound processing apparatus as claimed in claim 11, wherein

a heat exchanger for exchanging heat between the exhaust gas exhausted from said catalyst layer and water, and generating said steam is provided between said catalyst layer and said cooling apparatus.

21. A perfluoride compound processing apparatus as claimed in claim 11, further comprising

a cartridge, wherein said catalyst layer is formed inside, and
a casing wherein said cartridge is attached detachably, wherein
said heater, said casing, and said cooling apparatus are formed in an integral body structure in the above order.

22. A perfluoride compound processing apparatus as claimed in claim 21, further comprising

a reactor which comprises said cartridge, an internal tube wherein said cartridge is contained, and said casing, wherein
said casing of said reactor is shared with a casing of said heater.

23. A perfluoride compound processing apparatus as claimed in claim 14, wherein

an exhaust gas inlet portion for supplying said exhaust gas containing a perfluoride compound and a silicon component to said silicon component removing apparatus is extended into said silicon component removing apparatus, and
a gas outlet opening of said exhaust gas inlet portion is provided at a position lower than said spray apparatus, and said gas outlet opening is oriented downwards in said silicon component removing apparatus.

24. A perfluoride compound processing apparatus as claimed in claim 23, wherein

a diffusion portion for diffusing sprayed water from said spray apparatus is provided inside said silicon component removing apparatus between said spray apparatus and said exhaust gas inlet portion.

25. An exhaust gas processing apparatus of semiconductor manufacturing apparatus comprising:

a silicon component removing apparatus for removing a silicon component from an exhaust gas containing a perfluoride compound and said silicon component,
a heating apparatus for heating said exhaust gas containing said perfluoride compound, whereto any of water and steam is added after exhausted from said silicon component removing apparatus,
a catalyst layer filled with a catalyst for decomposing said perfluoride compound contained in said exhaust gas exhausted from said heating apparatus, and
a cooling apparatus for cooling said exhaust gas exhausted from said catalyst layer.

26. An exhaust gas processing apparatus of semiconductor manufacturing apparatus as claimed in claim 25, wherein

said heating apparatus, said catalyst layer, and said cooling apparatus are formed in an integral body structure in the above order, and
said integral body structure of said heating apparatus, said catalyst layer, and said cooling apparatus is installed in a building, wherein said semiconductor manufacturing apparatus is installed.

FIG. 3

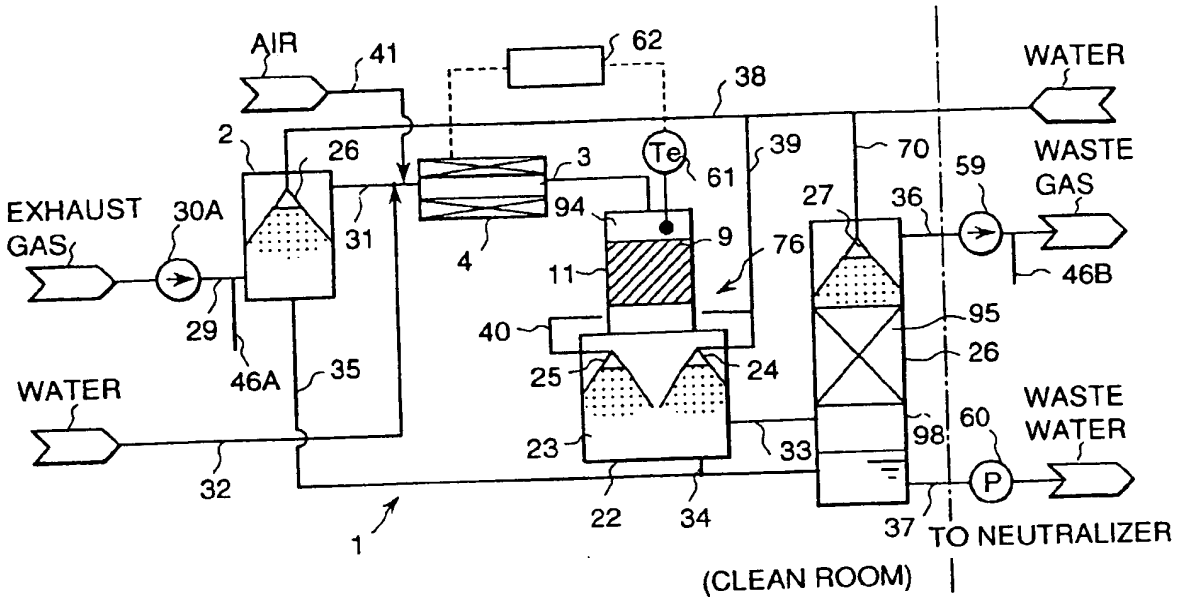

AIR
41
62
38
WATER
2
26
3
Te
61
39
70
WASTE
GAS
59
EXHAUST
GAS
30A
31
94
27
36
4
11
9
76
46B
29
40
95
46A
35
25
24
26
WATER
23
33
98
60
WASTE
WATER
32
22
34
37
TO NEUTRALIZER
1
(CLEAN ROOM)

FIG. 4

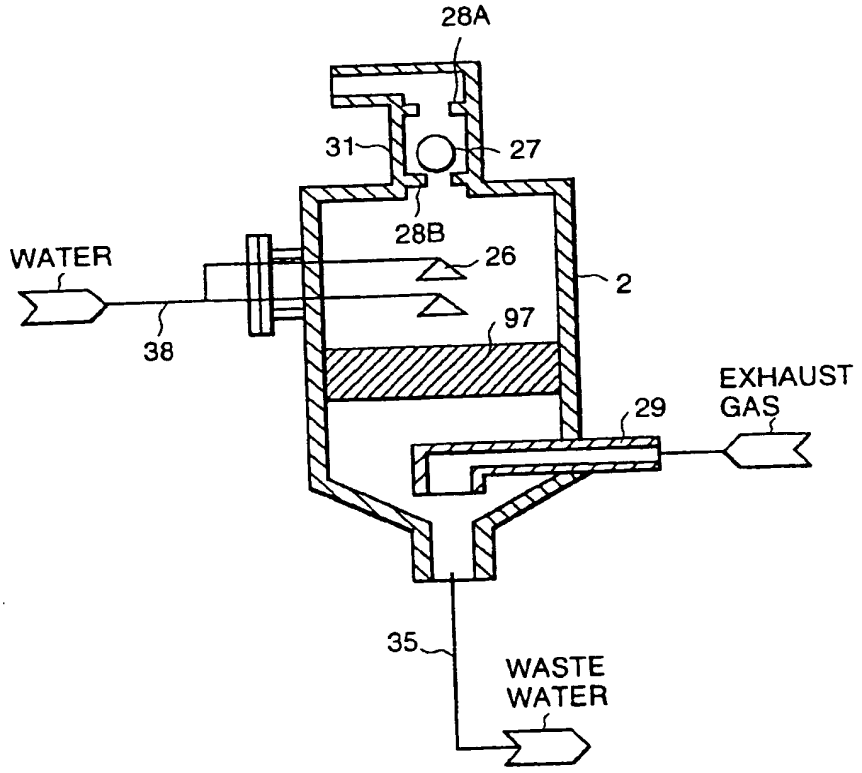

28A
31
27
28B
WATER
26
2
97
38
EXHAUST
GAS
29
35
WASTE
WATER

FIG. 6

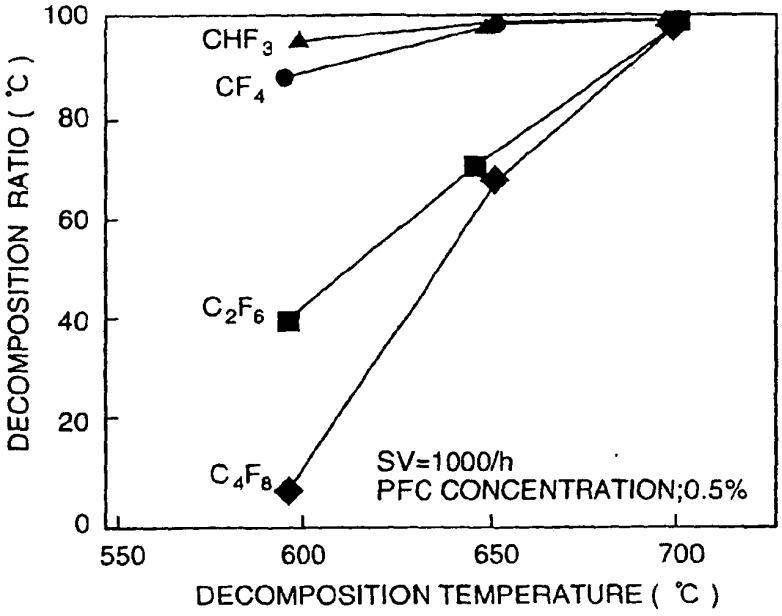

100
80
60
40
20
0
DECOMPOSITION RATIO (℃)
CHF3
CF4
C2F6
C4F8
SV=1000/h
PFC CONCENTRATION;0.5%
550
600
650
700
DECOMPOSITION TEMPERATURE (℃)

FIG. 7

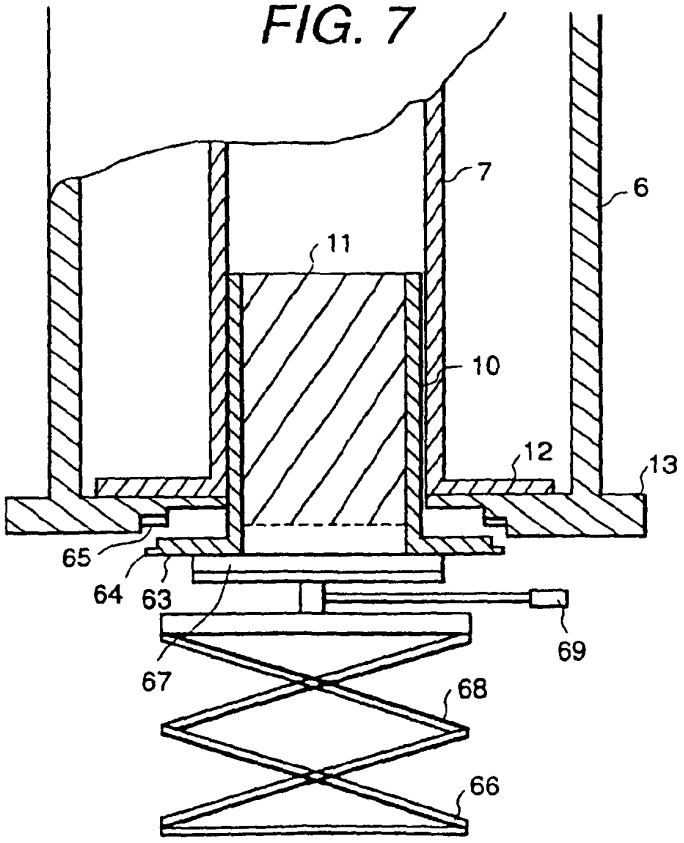

7
6
11
10
12
13
65
64
63
69
67
68
66

FIG. 10

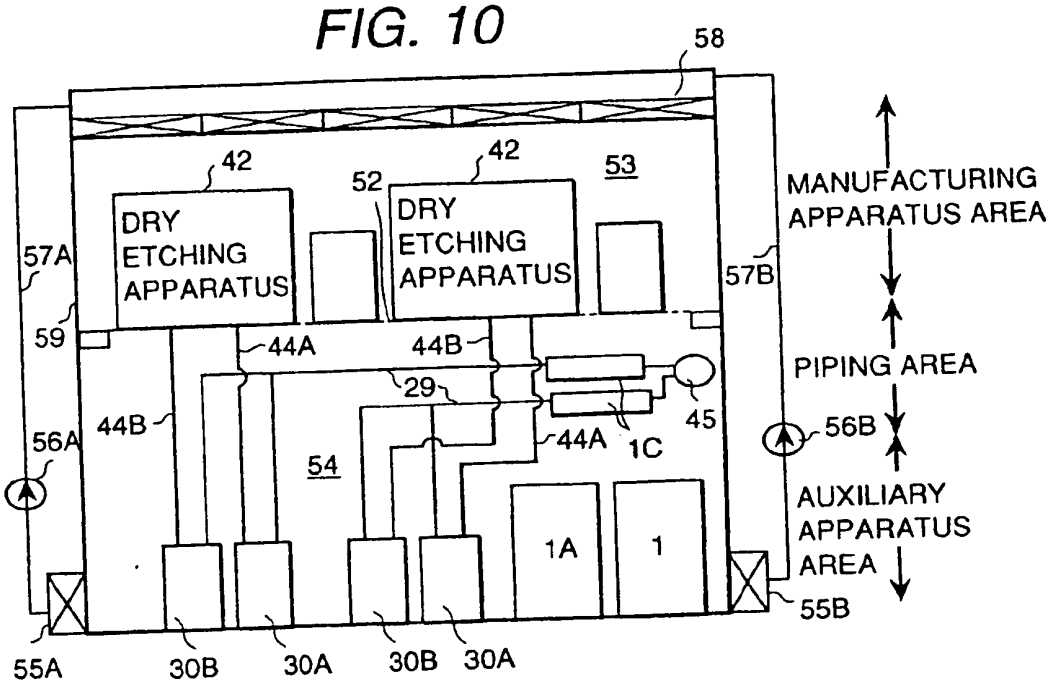


FIG. 11

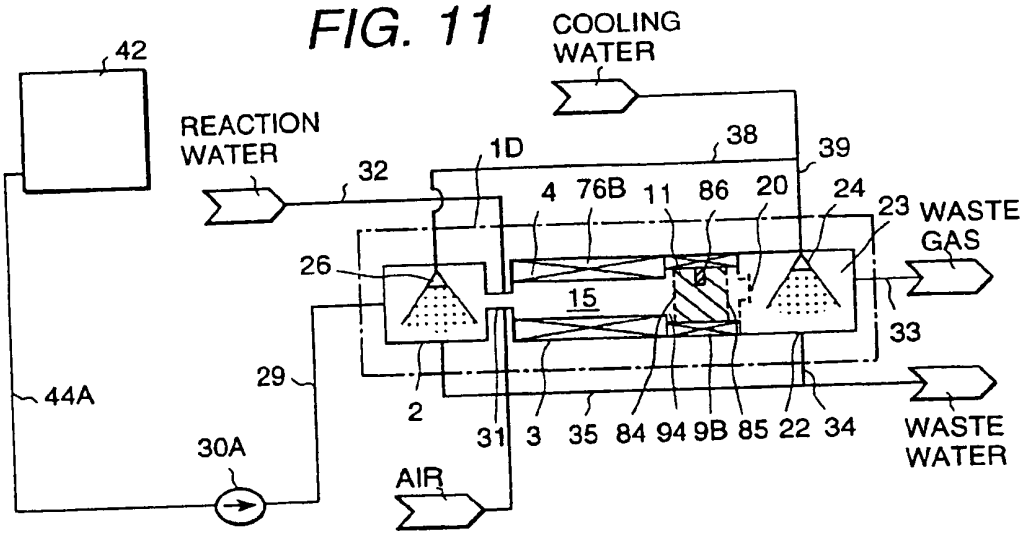
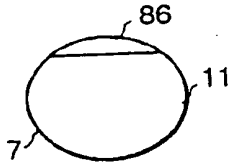


FIG. 12



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 916 388 A3

(12) EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
08.12.1999 Bulletin 1999/49

(43) Date of publication A2:
19.05.1999 Bulletin 1999/20

(21) Application number: **98309136.4**

(22) Date of filing: **09.11.1998**

(51) Int Cl.[6]: **B01D 53/86**, B01D 53/14, H01L 21/00

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **14.11.1997 JP 31308997**
27.05.1998 JP 14574898

(71) Applicants:
- **Hitachi, Ltd.**
 Chiyoda-ku, Tokyo 101-8010 (JP)
- **Hitachi Engineering Co., Ltd.**
 Hitachi-shi, Ibaraki 317-0073 (JP)
- **Hitachi Kyowa Engineering Co., Ltd.**
 Hitachi-shi, Ibaraki 317-0072 (JP)

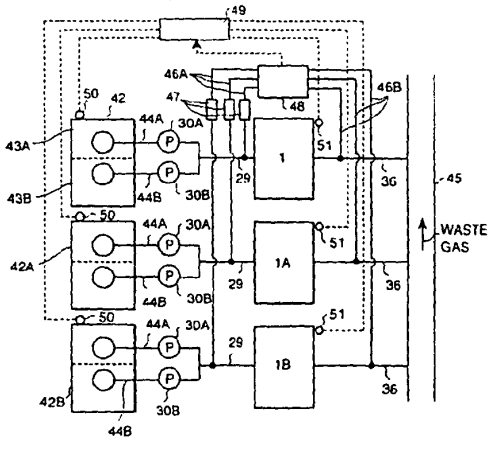
(72) Inventors:
- **Irie, Kazuyoshi**
 Hitachi-shi, Ibaraki 317-0077 (JP)
- **Mori, Toshihiro**
 Naka-gun, Ibaraki 319-1112 (JP)
- **Yokoyama, Hisao**
 Hitachioota-shi, Ibaraka 313-0038 (JP)
- **Tomiyama, Takayuki**
 2-chome, Hitachi-shi, Ibaraki 316-0004 (JP)
- **Takano, Toshihide**
 Nishiibaraki-gun, Ibaraki 309-1738 (JP)
- **Tamata, Shin**
 Higashiibaraki-gun, Ibaraki 311-1301 (JP)
- **Kanno, Shuichi**
 Hitachi-shi, Ibaraki 319-1225 (JP)

(74) Representative: **Hackney, Nigel John et al**
Mewburn Ellis,
York House,
23 Kingsway
London WC2B 6HP (GB)

(54) A method for processing perfluorocarbon and an apparatus therefor

(57) An exhaust gas containing a perfluoride compound (PFC) and SiF_4 is conducted into a silicon remover and contacted with water. A reaction water supplied from a water supplying piping and air supplied from an air supplying piping are mixed with the exhaust gas exhausted from the silicon remover. The exhaust gas containing water, air, and CF_4 is heated at 700 °C by a heater. The exhaust gas containing PFC is conducted to a catalyst layer filled with an alumina group catalyst. The PFC is decomposed to HF and CO_2 by the catalyst. The exhaust gas containing HF and CO_2 at a high temperature exhausted from the catalyst layer is cooled in a cooling apparatus. Subsequently, the exhaust gas is conducted to an acidic gas removing apparatus to remove HF. In accordance with the present invention, the silicon component is removed from the exhaust gas before introducing the exhaust gas into the catalyst layer. Therefore, surface of the catalyst can be utilized effectively, and the decomposition reaction of the perfluoride compound can be improved.

FIG. 1



EP 0 916 388 A3

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 98 30 9136

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

14-10-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0885648 A	23-12-1998	JP 11070322 A	16-03-1999
JP 63291625 A	29-11-1988	NONE	
US 5649985 A	22-07-1997	US 5716428 A	10-02-1998
EP 0642809 A	15-03-1995	AT 404431 B	25-11-1998
		AT 181993 A	15-04-1998
		US 5710359 A	20-01-1998

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office No. 12/82